

10-
46-

**This Page Is Inserted by IFW Operations
and is not a part of the Official Record**

BEST AVAILABLE IMAGES

**Defective images within this document are accurate representations of
the original documents submitted by the applicant.**

Defects in the images may include (but are not limited to):

- **BLACK BORDERS**
- **TEXT CUT OFF AT TOP, BOTTOM OR SIDES**
- **FADED TEXT**
- **ILLEGIBLE TEXT**
- **SKEWED/SLANTED IMAGES**
- **COLORED PHOTOS**
- **BLACK OR VERY BLACK AND WHITE DARK PHOTOS**
- **GRAY SCALE DOCUMENTS**

IMAGES ARE BEST AVAILABLE COPY.

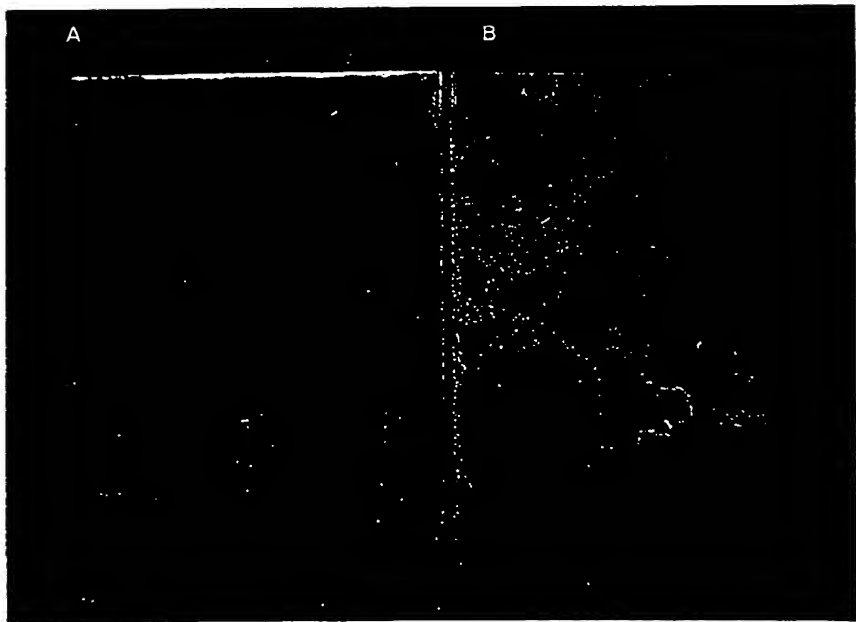
**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁷ : B01J 37/02	A1	(11) International Publication Number: WO 00/32311 (43) International Publication Date: 8 June 2000 (08.06.00)
(21) International Application Number: PCT/GB99/03858 (22) International Filing Date: 22 November 1999 (22.11.99) (30) Priority Data: 9826486.4 3 December 1998 (03.12.98) GB (71) Applicant (for all designated States except US): JOHNSON MATTHEY PUBLIC LIMITED COMPANY [GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London SW1Y 5BQ (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): LANZUELA DE ALVARO, Francisco [ES/GB]; 3 Main Prize Road, Bracknell RG12 2RE (GB). MALDE, Chandresh, Nemchand [GB/GB]; 37 Lower Henley Road, Caversham, Reading RG4 5LD (GB). PETCH, Michael, Ian [GB/GB]; 57 Barnsdale Road, Reading RG2 7JG (GB). (74) Agent: WISHART, Ian, Carmichael; Johnson Matthey Technology Centre, Blounts Court, Sonning Common, Reading RG4 9NH (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: IMPROVEMENTS IN COATINGS <div data-bbox="397 1150 1247 1768"></div> (57) Abstract <p>A substrate, such as a plate or catalyst monolith, may be coated with a metal oxide, particularly with a zeolite, by treating the substrate with a polyelectrolyte to form a coating, and then depositing the coating of metal oxide from an aqueous slurry. A continuous coating, which may incorporate many layers, can easily be formed. In the examples polyacrylamide is used as polyelectrolyte.</p>		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Larvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon			PL	Poland		
CN	China	KR	Republic of Korea	PT	Portugal		
CU	Cuba	KZ	Kazakstan	RO	Romania		
CZ	Czech Republic	LC	Saint Lucia	RU	Russian Federation		
DE	Germany	LI	Liechtenstein	SD	Sudan		
DK	Denmark	LK	Sri Lanka	SE	Sweden		
EE	Estonia	LR	Liberia	SG	Singapore		

5

IMPROVEMENTS IN COATINGS

This invention concerns improvements in coatings, and more especially concerns improvements in methods of coating metal oxides and the like onto metallic or non-metallic substrates.

10

It is very well established to coat metal oxides, such as alumina, ceria, zirconia, etc, as single or mixed oxides, onto metal substrates and ceramic such as honeycomb through-flow catalyst supports, used in huge numbers in exhaust gas catalysts. This is generally achieved by admixing the metal oxide into an aqueous slurry together with suitable components including adhesion modifiers, of which the "Ludox" (Trade Mark) silica is an example, to form a washcoat slurry. The substrate is then dipped or drenched in the slurry, and fired to yield a high surface area base for the catalyst. The silica may form 50 wt% or more of the solids content of the slurry, and this clearly dilutes the interaction between the catalyst metals and the oxide, which is very important. There has not been significant improvement in these coating techniques for some 20 or 30 years, yet the design of exhaust gas catalysts is becoming more sophisticated and demanding, requiring new components such as zeolites and other multi-layers to be incorporated. We believe that traditional coating methods are failing to deal with new requirements, and in particular, traditional coating methods give problems in multi-layer coating.

25

We have previously disclosed the use of polyelectrolytes to coat catalyst particles etc with zeolites formed simultaneously *in situ* (see EP 878 233). We have now discovered that polyelectrolytes can be used to pre-treat metal and ceramic substrates without such *in situ* formation of the zeolites, in a process in which one or more pre-formed metal oxides, including zeolites and the like, is deposited onto the substrate, and not only is a sound, even coating obtained without requiring dilution with adhesion modifiers, (but may include such adhesion modifiers) but the coating is especially suitable for the deposition of further coatings of similar or differing type.

35

Accordingly, the present invention provides a method of depositing metal oxide coatings onto a substrate, which comprises treating the surface of said substrate with a polyelectrolyte to yield a surface coating of the polyelectrolyte thereon, and subsequently

or simultaneously treating the coated surface with an aqueous slurry comprising metal oxide particles. If required, additional layers of the same or different metal oxide may be applied, either to increase the loading of the metal oxide or to form a multilayer coating.

Desirably, the polyelectrolyte is applied in the form of an aqueous solution, eg a 0.01 to 20 wt% solution, in the case of the materials specifically described hereinafter a 4 wt%, solution has been found satisfactory. The polyelectrolyte may be any suitable polyelectrolyte, eg anionic or cationic, but polyacrylamides are suitable, such as "Alcostat" (Trademark) 167 available from Allied Colloids Ltd, England. Other polyacrylamides may be considered. For such materials, desirably, the solution is alkaline, for example of pH of approximately 9. Routine testing to optimise the solution pH for each substrate and polyelectrolyte should be undertaken, and may be acid or alkaline, primarily depending upon the surface chemistry of the substrate. Treatment of the substrate may be by any suitable method, including spraying, dipping, vacuum application, drenching using a "waterfall" and the like, and may be carried out at room temperature. Desirably, the polyelectrolyte solution is dried to form a continuous surface polymer layer.

The substrate may be any metal or ceramic material, in any form, including particularly honeycomb through-flow catalyst supports, but also devices of the type known as static mixers, which provide good gas or other fluid mixing. The metal may be, for example, a stainless steel, including "Fecralloy" or aluminium, and the ceramic may be cordierite or the like. Other substrates which require, or may be protected by, an oxide coating, should also be considered.

25

The term metal oxide includes zeolites of all types and of all Si to Al ratios, and includes modified, eg ion-exchanged zeolites, as well as "Silicate" and recently-available zeolite-type compositions where Ga and In or other suitable metals are incorporated into the zeolite framework structure and single or mixed oxides, for example selected from one or more of ceria, zirconia, magnesia, alumina and silica. The metal oxide is desirably in the form of an aqueous slurry, eg of about 40 wt% solids content of particles of the appropriate particle size; if necessary the metal oxide may be milled to disperse the metal oxide whilst simultaneously size reducing. The slurry may, but need not, include an

adhesion modifier, and may include other components including catalytically active particles and solutions of catalytically active metals and/or promoters therefor.

The slurry is then suitably applied by any method to the polyelectrolyte-coated substrate, and is then suitably dried. A final stage is desirably firing, or calcining, to firmly deposit the oxide coating on the substrate. Before the final firing, however, additional slurries of oxide and/or other components may be deposited, to result in a continuous or thicker coating, or a multi-component series of coatings. If desired or necessary, a further polyelectrolyte layer may be applied, and one or more additional metal oxide or other coatings may be applied.

In an alternative embodiment, the polyelectrolyte is admixed with the slurry without a separate pre-coating step. Otherwise the process and materials considerations are fairly similar. This embodiment is expected to be particularly suitable for depositing a thin, even coating.

It is believed, although we do not wish to be bound by any theory, that the polyelectrolyte acts to reverse the charge on the substrate, thus permitting the slurry particles to adhere firmly, and we believe that upon deposition of a second coating, the polyelectrolyte is "re-activated" and serves to cause excellent adhesion of the second coating.

It is believed that the present invention has significant and unexpected benefits in achieving good coatings on substrates that have previously been difficult to coat, and in particular permits sound and adherent two or multi-layer coatings.

The present invention is illustrated by the following examples.

EXAMPLE 1

30

An aluminium plate is soaked with aqueous 4 wt% polyacrylamide solution at pH 9. The wet plate is then dried to leave a thin surface coating of polyelectrolyte. The coated plate is dipped into a standard zeolite x,y washcoat slurry as used in the

exhaust gas catalyst industry, containing 40 wt% zeolite, with the pH adjusted to between 8 and 9. The washcoat adheres to the plate, and the coated plate is removed and dried at 100 °C for 30 minutes. A further identical washcoat layer was then applied to deposit a desired thickness. The coated metal plate is then calcined at 400 °C for 2 hours, which removes the polyelectrolyte residue. A photograph of the thus-coated plate ("A") is shown in the accompanying drawing page. For comparison, the identical procedure was followed without the polyelectrolyte treatment. Although a first coating appeared successful and even, a second coating caused the combined coating to dramatically peel; a photograph of the coated plate is shown as "B" in the drawing. It can readily be seen that the present invention permits an even and continuous coating, whereas double coating without the polyelectrolyte results in flaking of the coating, and uneven, discontinuous coating.

Although the above Example utilised a 100% zeolite coating, other successful coatings can be applied with 50 wt% "Ludox" silica adhesion modifier, or any other proportion.

EXAMPLE 2

Zeolite 13X on Aluminium Sheet

An aluminium sheet was coated with zeolite 13X (Zeolyst Int.) using a polyelectrolyte aqueous solution (5% of Allied Colloids BLO6272AQ/Alcostat167, SD n°0004568, and pH 9-10). After having fired the aluminium plate at 200°C, it was anodised in a 15% sulphuric acid solution. The plate was then coated with a thin layer of polyelectrolyte, then four consecutive passes of zeolite 13X were applied with a total weight gain of 0.57g over a surface of approximately 5 in² (32 cm²); this represented a loading improvement over 3 times greater than could be achieved in previous experiments. Between the third and the fourth passes, a second layer of polyelectrolyte was necessary. Finally, the sheet was calcined at 300°C to burn off the polyelectrolyte.

EXAMPLE 3

Zeolite 13X on Aluminium Monoliths

Two aluminium honeycomb monoliths of different cell density (400 and 200 cells

per sq.in) were coated with zeolite 13X using a polyelectrolyte aqueous solution (5% of Allied Colloids BLO6272AQ/Alcostat167, SD n° 00045768, and pH 9-10). The 400 and 200 cpsi monolith reached coatings of 2.7 and 3.2 g/in³ respectively in fourteen consecutive passes of zeolite 13X with very low percentages of binder (below 5%). A polyelectrolyte layer was applied prior to the first pass and between the 11th and the 13th passes.

EXAMPLE 4

Zeolite Y on Aluminium Sheet

10

An aluminium sheet was coated with zeolite Y (Zeolyst Int.) using a polyelectrolyte aqueous solution (5% of Allied Colloids BLO6272AQ/Alcostat167, SD n°00045678, and pH 9-10). The aluminium plate was coated with a thin layer of polyelectrolyte, then three consecutive passes of zeolite Y were applied with a total weight gain of 0.81g over a surface of approximately 1.55in² (10cm²); previous tests using this zeolite without polyelectrolyte showed that the coating would completely disintegrate and peel off after two passes.

EXAMPLE 5

Zeolite Y on Aluminium Monoliths

20

An aluminium honeycomb monolith of 200cps cell density was coated with zeolite Y using a polyelectrolyte aqueous solution (5% of Allied Colloids BLO6272AQ/Alcostat167, SD n° 00045768, and pH 9-10). A polyelectrolyte layer was applied prior to the first pass. The monolith reached coatings of 4.2g/in³ of zeolite Y in seven consecutive passes.

EXAMPLE 6

Zeolite 4A on "Fecralloy" static Mixers

30

Static mixers (obtainable from Sulzer) made of "Fecralloy" metal were pre-heated to 900°C for 1 hour and soaked in 5% wt Alcostat167 polyelectrolyte solution (Allied Colloids Ltd) at pH 9. The wet mixer is then dried to leave a thin surface polyelectrolyte

coating. The mixer is then dipped in a slurry containing 35wt% zeolite 4A with 5wt% platinum, and 2wt% Ludox silica (DuPont). Excess zeolite is removed by blowing the coated mixer through with 80psi of nitrogen. This helps to free any blocked channels in the mixer. The coated mixer is then dried at 120°C/8hrs, and calcined at 500°C/2hrs. The calcination step burns off the polyelectrolyte layer, and leaves the zeolite coating intact. In this case it results in a thick zeolite layer with coating density of 3.1 ginch⁻³ throughout the mixer.

EXAMPLE 7

Alumina -based Catalyst on "Fecralloy" static Mixers

A static mixer was coated, using the same methodology as in Example 6 with 5% Pt, 0.1%Fe on alumina catalyst. This catalyst was mixed with 7% Dispersal binder (Condea), and made into a 35wt% aqueous washcoat. The resultant coating was observed to have good cohesion and integrity. A coating density of 3.7 ginch⁻³ was achieved.

EXAMPLE 8

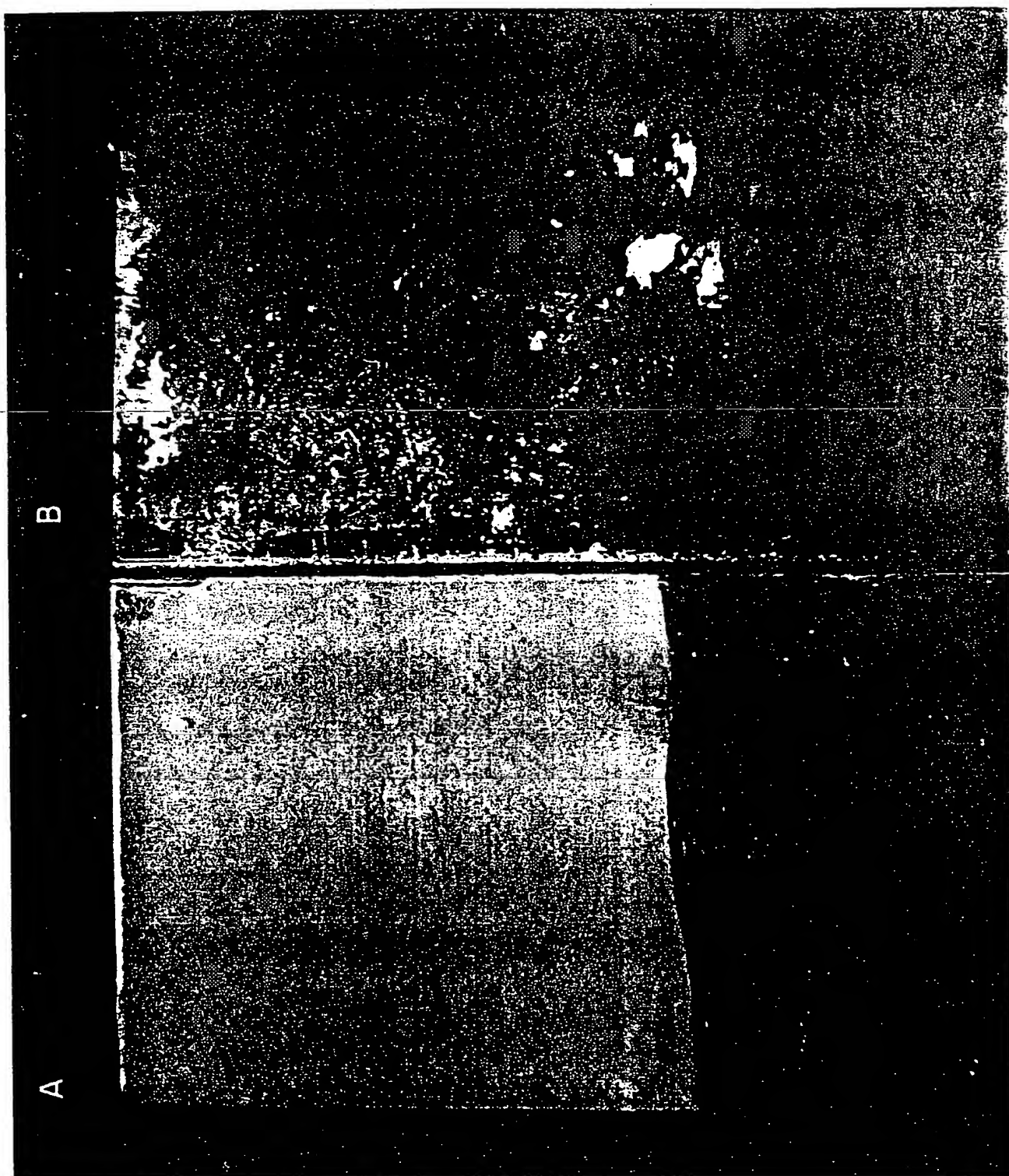
Zeolite H-ZSM-5 on Ceramic Monolith

A conventional cordierite monolith was successfully coated with H-ZSM-5 synthetic zeolite using the technique of Example 3. The test was repeated successfully using a mixture of zeolite and colloidal silica binder.

The invention may be modified by the skilled person without departing from the scope thereof.

CLAIMS

1. A method of depositing metal oxide coatings onto a substrate which comprises treating a surface of said substrate with a polyelectrolyte to yield a surface coating of the polyelectrolyte thereon, and subsequently or simultaneously treating the coated surface with an aqueous slurry comprising metal oxide particles.
2. A method according to claim 1, wherein said polyelectrolyte is a polyacrylamide.
3. A method according to claim 1 or 2, wherein the substrate is a metal or ceramic catalyst support substrate in plate or monolith form.
4. A method according to claim 1, 2 or 3, wherein the metal oxide is a zeolite.
5. A method according to claim 1, 3 or 4, wherein the metal oxide is selected from alumina, silica, ceria, zirconia, magnesia and mixed oxide catalyst supports.
6. A method according to claim 4 or 5, wherein the metal oxide incorporates a catalytic component.
7. A method according to claim 6, wherein the catalytic component is one or more of the platinum group metals.
8. A supported catalyst comprising a plate or monolith coated with a metal oxide, produced according to any one of the preceding claims.



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 99/03858

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 B01J37/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DE 35 26 383 C (DIDER-WERKE AG) 11 December 1986 (1986-12-11) example 1 column 2, line 60 -column 3, line 63	1,3,4,6, 8
X	DE 23 00 932 A (FUJI PHOTO FILM CO LTD) 19 July 1973 (1973-07-19) the whole document	1,2,5
A	EP 0 266 257 A (RHONE POULENC CHIMIE) 4 May 1988 (1988-05-04)	1,3,5-8

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search

28 February 2000

Date of mailing of the international search report

10/03/2000

Name and mailing address of the ISA

European Patent Office, P.B. 6818 Patentean 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Zuurdeeg, B

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern. Patent Application No

PCT/GB 99/03858

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 3526383 C	11-12-1986	AT 38941 T DD 248517 A EP 0213271 A ES 2000470 A US 4806427 A	15-12-1988 12-08-1987 11-03-1987 01-11-1991 21-02-1989
DE 2300932 A	19-07-1973	JP 48075295 A	11-10-1973
EP 0266257 A	04-05-1988	FR 2605531 A DK 558887 A JP 63178850 A US 4891350 A	29-04-1988 28-04-1988 22-07-1988 02-01-1990